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# Proceedings of the

# CONFERENCE ON ADVANCES IN FLAVOR RESEARCH

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~~Held at~~ New Orleans, Louisiana
~~March 25 and 26~~, 1963

AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

# CONFERENCE ON ADVANCES IN FLAVOR RESEARCH

New Orleans, Louisiana
March 25-26, 1963

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(A list of those attending the conference is in the Appendix.)

# CONTENTS

Foreword . . . . . . . . . . . . . . . . . . . . . . . . . . . . . i

Program. . . . . . . . . . . . . . . . . . . . . . . . . . . . . ii

Psychological Methods for Measuring Flavor Effects
David R. Peryam. . . . . . . . . . . . . . . . . . . . . . . . . 1

The Improvement of Flavor
William J. Downey. . . . . . . . . . . . . . . . . . . . . . . . 4

Cooperative Research Between the Florida Citrus Commission and University of Florida Citrus Experiment Station on Volatile Flavor Constituents of Citrus Juices
Richard W. Wolford . . . . . . . . . . . . . . . . . . . . . . . 6

Some Investigations of the Chemistry of Flavor
Emily L. Wick. . . . . . . . . . . . . . . . . . . . . . . . . . 10

The Relation of Molecular Spacial Configuration to Flavor and Physiological Properties
Carl Bordenca. . . . . . . . . . . . . . . . . . . . . . . . . . 11

Spectrometry in Identification of Flavor Components; Application to Small Samples
R. M. Silverstein. . . . . . . . . . . . . . . . . . . . . . . . 11

Progress and Limitations in the Identification of Flavor Components
William S. Ryder . . . . . . . . . . . . . . . . . . . . . . . . 12

The Volatile Flavor Substances of Celery
Harvey J. Gold . . . . . . . . . . . . . . . . . . . . . . . . . 15

Chemistry of Meat Flavor
Irwin Hornstein. . . . . . . . . . . . . . . . . . . . . . . . . 17

Gas Chromatographic Studies on Volatile Compounds from Processed Tomatoes
Richard E. Hein. . . . . . . . . . . . . . . . . . . . . . . . . 18

Studies on the Flavor of Allium
R. A. Bernhard . . . . . . . . . . . . . . . . . . . . . . . . . 20

Preliminary Studies on the Flavor of Roasted Peanuts
George R. Waller . . . . . . . . . . . . . . . . . . . . . . . . 22

Summary Remarks on Conference
M. K. Veldhuis . . . . . . . . . . . . . . . . . . . . . . . . . 23

Appendix . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25

# FOREWORD

The Conference on Advances in Flavor Research was sponsored by the Southern Utilization Research and Development Division in cooperation with the southern agricultural experiment stations. Its purpose was to strengthen liaison between the Southern Division and the experiment stations, and to exchange information on important subjects of joint interest.

In prior years attendance at the annual conference of these cooperating agencies has been confined to their representatives. The topic of flavor, however, aroused interest throughout the country; therefore, the Southern Division joined the southern experiment stations in encouraging the attendance of anyone interested in the area of flavor research.

This report which was compiled by Leah C. Berardi and Beatrice A. Sharar of this Division, summarizes the statements of the various speakers during the conference, and gives an account of the discussions which followed. If further details regarding any particular subject are desired, they may be obtained by communicating with the person concerned.

C. H. Fisher
Director, Southern Utilization Research and Development Division

The statements contained in the speeches reproduced in these proceedings of the Conference are those of the speakers and do not necessarily indicate or reflect the views of the U. S. Department of Agriculture. Mention of products does not constitute their endorsement by the U. S. Department of Agriculture over others of similar nature that are not mentioned.

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# PROGRAM

Conference Room - Third Floor
Monday, March 25, 1963

8:30 a.m. Registration

| | |
|---|---|
| 9:00 a.m. Introduction | E. L. Patton<br>Assistant Director, SU |
| Welcome | C. H. Fisher<br>Director, SU |
| Opening Remarks | J. J. Mikell<br>Assistant Director<br>Louisiana Agr. Exp. Sta. |

Presiding: Vernon H. McFarlane, Chief, Food Crops Laboratory, SU

| | |
|---|---|
| Psychological Methods for Measuring Flavor Effects | David R. Peryam<br>U.S. Army Quartermaster Research and Engineering Command |
| The Improvement of Flavor | William J. Downey<br>Fritzsche Brothers, Inc. |
| Cooperative Research Between the Florida Citrus Comm. and Univ. of Florida Citrus Experiment Sta. on Volatile Flavor Constituents of Citrus Juices | Richard W. Wolford<br>Florida Citrus Commission |

12:30 p.m. Luncheon

1:30 p.m.

Presiding: A. E. Denton, Director, Basic Research, Campbell Soup Co.

| | |
|---|---|
| Some Investigations of the Chemistry of Flavor | Emily L. Wick<br>Massachusetts Institute of Technology |
| The Relation of Molecular Spacial Configuration to Flavor and Physiological Properties | Carl Bordenca<br>The Glidden Company |
| Spectrometry in Identification of Flavor Components; Application to Small Samples | R. M. Silverstein<br>Stanford Research Institute |

| | |
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| Progress and Limitations in the Identification of Flavor Components | William S. Ryder<br>General Foods Corporation |

9:30 a.m., Tuesday, March 26, 1963

Presiding: Herman J. Reitz, Horticulturist in Charge, Citrus Experiment Station.

| | |
|---|---|
| The Volatile Flavor Substances of Celery | Harvey J. Gold<br>U.S. Fruit & Veg. Prod. Lab. |
| Chemistry of Meat Flavor | Irwin Hornstein<br>Meat Lab., EU |
| Gas Chromatographic Studies on Volatile Compounds from Processed Tomatoes | Richard E. Hein<br>Mellon Institute |
| Studies on the Flavor of Allium | R. A. Bernhard<br>California Agr. Exp. Sta. |
| Preliminary Studies on the Flavor of Roasted Peanuts | George R. Waller<br>Oklahoma State University |
| Summary Remarks on Conference | M. K. Veldhuis<br>U.S. Fruit & Veg. Prod. Lab. |

Adjournment

Tour of Research Facilities - Southern Utilization Research and Development Division

# PSYCHOLOGICAL METHODS FOR MEASURING FLAVOR EFFECTS

by
David R. Peryam
Armed Forces Food & Container Institute
U. S. Army Quartermaster Research and Engineering Command

Flavor, taste, odor, texture, etc., are often considered as properties of foods, but it is more valid to look on them as properties of people's behavior. They arise from physical stimuli, but the stimuli are not the properties. Usually interest is focused not on description of foods, but on its acceptance evaluation. Psychology is a primary source for guidance; however, until recently psychologists have not contributed in a major way to the solution of practical problems. Because the data dealt with in sensory evaluation tend to be variable, the statistical approach is important if effective work is going to be accomplished. However, one also needs knowledge about the human behavior itself.

Methodology is the key factor in psychological measurement. Tests can be classified according to the kind of psychological functioning required of the subject, as: (a) Affective tests based on preference, pleasure-displeasure, like-dislike; (b) Discriminative tests based on judgment, which may be concerned with difference _per se_, or difference on a specified dimension; (c) Descriptive tests requiring the sorting out of the many separable qualitative dimensions which explain people's differential behavior toward products.

Tests can be classified according to form, as: Paired comparisons, rank order, rating scale, discrimination tests, attribute identification, and descriptive analysis.

Physical measurement depends upon objectively real standards simultaneously present; in contrast, the standards in psychological measurement frequently rely on memory. Some examples are: (a) Standard physically present in the test situation and so designated, (b) standard physically present for reference but not part of the formal test, (c) standard represented by general attitudes.

An important feature in the design of a sensory test is the dimension of evaluation, which must be clearly defined. Some dimensions are easily understood, but others may be interpreted in different ways by different people, or may have meaning only to panel members who have had special training.

The sampling of people to participate in tests is an unsolved problem. Procedures are available for drawing proper samples but seldom are applied in the laboratory context. Such panels are believed to be fairly representative of the general population, and this can sometimes be empirically verified; however, there is no assurance of this fact. Spending a great deal of effort on the selection and training of test subjects is unwarranted, since it is not possible to select and train for all of the characteristics which are important in good performance.

## DISCUSSION

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|---|---|
| Question: | Is there a single best psychological method which you would recommend for measuring flavor effects? |

Dr. Peryam: I do not think any single method should be used for all purposes. It depends upon the problem; different purposes call for different approaches. The scientist should determine what kind of information he wants about the material to be tested, then select a method and design the experiment on this basis. Often the difficulty is that the experimenter wants several different kinds of information about a given set of samples and tries to get it all in one test. This may lead to total failure, i.e., he gets no straightforward answer to any question.

Question: What is the explanation of the situation where A is preferred to B; B is preferred to C; but then C is preferred to A?

Dr. Peryam: This is a phenomenon more often alleged than proven; however, such logically contradictory results are sometimes obtained. Several possible explanations have been offered, although, again, none are proven. Such an effect may be related to faulty test design coupled with failure to recognize and account for the probable sources of variability. For example, if the AB pair is tested one day, the BC pair another day, and the AC pair at still another time, the apparent contradiction might arise because different people have been used each time or because of some operational error in one of the tests. Another explanation would accept the "circularity" of the preference as real and depends upon the existence of special effects, or contrasts, among the samples. For example, certain properties of Sample A cause it to be preferred to Sample B when the two are presented together and certain properties of Sample B cause it to be preferred to Sample C when that pair is presented; however, when the AC pair is presented, a different situation arises. People now pay attention to qualities not previously noticed, or considered as unimportant and their criteria for the preference judgment may change. Note, also, that the demonstration of this phenomenon may depend on the paired-comparison method. You are less likely to find it when using a rating scale.

Question: When descriptive terms are requested, would it be best to attempt to train the panel in the use of a few specific terms in describing the particular sensory phenomena they might encounter and restrict them to the use of these terms only?

Dr. Peryam: This is a matter of opinion, but my answer is that it would be better. One tries to limit variability and one way to do it is to restrict test subjects to specific descriptive categories. Limit the hypotheses you make about your samples and you can expect more reliable information. Most everyone can detect a floral odor, but you probably would have to train panel members to detect specific differences among various types of floral odors. Concentrate on helping subjects limit variability by being more precise in descriptions. However, restriction to specific categories has certain disadvantages. The panel members can describe the samples only according to the descriptive terms you have provided, which sometimes may not be complete. You must have a definite objective in setting up your list of terms.

Question: What evidence do we have about the relation between physiological differences, such as sensitivity to PTC (phenyl thiocarbamide) and preference for food?

Dr. Peryam: There is a lot of supposition about such differences, and I am sure there are some real effects; however, for the most part they have not been clearly delineated. Specifically, as to PTC (phenyl thiocarbamide), in a paper given by Dr. A. L. Fox at the National American Chemical Society meeting in 1954, he reported that he was able to classify people on the basis jointly of their ability to taste PTC and whether they perceived sodium benzoate as salt, sweet, sour, bitter, or tasteless. Further, he reported very definite relationships between this classification and preference for various types of foods. Subsequently, experimental work by other people has been unable even to confirm Fox's method of classification, let alone the relation to preferences. But this is only one type of physiological difference. Certainly, we know that some physiological differences will alter preferences; e.g., starvation, metabolic deficiencies, endocrine disturbances. But, aside from conditions that might be called abnormal, there is little solid evidence. In the typical situation where we are using normal consumers in our tests, there is not much we can, or should, try to do about physiological differences.

Question: What pattern of psychological testing of flavor is appropriate for a small manufacturer to utilize in his product development?

Dr. Peryam: I can't answer without knowing the product and especially the level of his interest. Much depends upon whether one is branching into new product development. If interest lies only in better quality control of standard products, including the selection of raw materials and redesign of processes, this may be adequately handled by small panels in the laboratory. But, if broader patterns of change are planned, such as the development of entirely new products, this may call for testing with larger groups of consumers, preferably from outside of your own company. Small laboratory panels are appropriate in the initial phases, but their information needs to be supported by other approaches.

Question: How can you derive direction to flavor development work in view of the inarticulateness of the inexpert panelist--i.e., the consumer? Have you ever placed a better vocabulary in such subject's hands?

Dr. Peryam: Well, I don't know whether you can. But the consumer is not completely inarticulate. He can tell you if he likes a product or does not like it. On the other hand, if you ask consumers what you can change in a product to make it more acceptable, they can't necessarily describe to you what is needed. Then the consumer is inarticulate. But why should you expect him to deal with your product in language that you can interpret immediately into process changes? This is your problem, not his. Yes, certain kinds of vocabulary can be used with consumers. For example, when asked to choose which cake mixes were more "chocolaty," they have been able to show that certain mixes were more "chocolaty" than others. But, you can't just toss out any vocabulary and expect meaningful results. You may provide a phrase or word which is not clear to them. You have to keep in mind the particular feature or property of the product you are describing and be sure that the consumer interprets the descriptive vocabulary as applying to the same feature or property. This is the difficult stage of the problem.

## THE IMPROVEMENT OF FLAVOR

by
William J. Downey
Fritzsche Brothers, Inc.

From the time that man first became aware of the possibility of improving the taste of food, undoubtedly by his charring a piece of meat, food technologists the world over have been striving to make our foods more palatable. Great strides have been made in the preparation of foods since these humble beginnings thousands of years ago--pasteurization; aseptic canning; dehydration; freezing; and, more recently, freeze drying and irradiation. All of these have given the food processor considerable versatility in the products he manufactures. At the same moment, the consuming public has been treated to foods in wide-ranging style and form. It is now possible for one to savor the exotic wares of the Orient or sample the spicy warmth of the Mediterranean as easily as he may enjoy the aroma and taste of homemade biscuits. International and intercontinental cuisine is no farther away than your local supermarket. Foods may be purchased fresh, canned, concentrated, frozen or powdered, packaged for immediate use or protected for prolonged storage. However the housewife may wish to satisfy her family's need, a variety of nutritious and flavorful products are available.

The flavoring industry has played a fundamental role in enhancing the taste of our nation's food supply, employing many different materials to accomplish this--spices, essential oils, oleoresins, botanical extracts, fruit juices, and aromatic chemicals. With these, flavors of almost unlimited type have been prepared, yet much remains to be done, much remains to be learned. There are, undoubtedly, certain constituents that affect flavor and aroma in fruits and spices which still remain hidden from the chemist, but the veil of mystery is slowly but surely being lifted. The introduction of instrumental methods of analysis with the universal usage of the spectrophotometer and chromatograph has been principally responsible for these advances. The analyst's skill has become ever more important to science's continued effort to improve flavor. Therefore, we intend to discuss the methods currently employed in this investigation and the development of flavoring compounds.

## DISCUSSION

Question: Have you experienced problems in the flavors of natural oils or juices, traceable to crop-control chemicals, i.e., insecticides, herbicides, and the like?

Mr. Downey: We have experienced some problems with pesticides, and so forth, but have not noted any effects on flavor. Naturally, we have been concerned with the amount of pesticide on the raw materials we handle. Studies we have conducted indicate that if the fruit is washed efficiently, the residue of surface chemicals is nil. Trace elements can greatly influence the quality of a flavor. Therefore, the control of such is one of our principal considerations.

Question: Do you know of any natural flavor which has been successfully synthesized?

Mr. Downey: I would say the chemist has been able to produce synthetic products which closely approximate the flavors of natural fruits. Strawberry, raspberry, and cherry flavors are good examples of such synthetics. Natural fruit flavors will vary in character, depending on source and type, and especially as to how they are used in a finished food. Often, natural flavors are not suitable for use in certain roles--for instance, the stone and berry fruits in hard candy. Synthetics overcome the difficulty of concentration and stability encountered here and are therefore relied upon for flavor in such an application. In bakery products, synthetic flavors once again perform a vital function, withstanding the high temperatures employed, an area where the natural counterpart would be sadly lacking. Although we now have many fine products, much remains to be accomplished in the development of natural-tasting synthetic-based flavors. This is why we appreciate and encourage the efforts of chemists like Dr.Wick and Mr. Wolford.

Question: You stated that the human tongue and nose were essential organs in evaluation of flavor. To what extent do you feel that the human eyes are used in evaluation of "taste?"

Mr. Downey: Undoubtedly, many of you visited the Fritzsche Brothers' display booth at the Institute of Food Technologists' Meeting in Miami. You will recall that we exhibited flavored candies that had colors not in keeping with their character--for instance, the cherry pieces were a green shade. Although each person was carefully informed of these discrepancies, the majority were misled by the color. The particular shade used had more influence on the judgment of the individual than the information being received by his olfactory nerve. Color definitely influenced the flavor evaluation. These simple tests amplify Dr. Peryam's remarks concerning the importance of color in the psychological measurement, and I might add identification, of flavor.

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| Question: | Don't you think with fruit and vegetables that work should begin with the plant breeding as far as flavors are concerned? |
| Mr. Downey: | You are quite right. This would be the most fundamental approach, and food processors are looking in this direction. However, one of their other requirements has been the high yield of product per acre; and this, unfortunately, has not always coincided with the development of a variety with the finest flavor. A similar program of plant breeding is currently being pursued in the spice field with a more pressing motivation--survival of raw-material sources. As the population of the world increases, the possibility that less acreage will be devoted to spices and more to food production will become a reality. Therefore, it behooves all of us in this field to increase our yields, improve our technology, and seek out new areas for cultivation of essential oil-bearing plants. Research in the field of genetics will become of paramount importance. |
| Question: | Are flavor components which are present in parts per billion or fraction parts per million really significant in flavor perception? |
| Mr. Downey: | Certain of the aromatic chemicals and essential oils employed in the construction of a flavor are extremely intense odorants. A minute amount of any of these will cause a significant sensation on the senses; and their contribution to total flavor effect, even when employed at such low levels, is notable. In this class, we can consider the mercaptans in coffee and the ionones in raspberry. |

## COOPERATIVE RESEARCH BETWEEN THE FLORIDA CITRUS COMMISSION AND UNIVERSITY OF FLORIDA CITRUS EXPERIMENT STATION ON VOLATILE FLAVOR CONSTITUENTS OF CITRUS JUICES

by
Richard W. Wolford
Florida Citrus Commission

Citrus processors are placing continued emphasis on maintaining good flavor in Florida processed citrus products, while simultaneously using a wider range of fruit varieties, increasing the yield of juice per box of fruit, and improving the physical stability of these products. Processing techniques favorable to one of these objectives are sometimes unfavorable to another; and, as a consequence, flavor maintenance is a significant problem. In addition, there is considerable interest in the development of new products such as dried citrus powders. Therefore, a basic understanding of flavors is deemed necessary to the maintenance and development of the best possible products.

A cooperative program of basic research on the volatile constituents associated with the flavor of citrus juices was initiated in 1957 and has had formal project status at the Citrus Experiment Station since June 1960.

With particular emphasis on orange juices, methods have been developed for recovery of volatile components as aqueous essences, and subsequently for their isolation and separation. With PTGC (programmed temperature gas chromatography) in excess of 55-component peaks have been shown using these essences. Additional analytical techniques including paper chromatography, infrared spectroscopy, and derivative formation have been employed in the identification of individual components. Positive identifications have been obtained for 29 constituents, and 14 additional constituents have received tentative identification employing retention data on 2 gas chromatographic columns. The employment of subtractive methods of analysis has permitted the separation and identification of the carbonyl components present in very low concentrations. Also, the adaptation of column adsorption chromatography has made possible the identification of the alcohols and allowed PTGC analysis of a mixed ester and terpene fraction. Some 22 esters, exclusive of ethyl butyrate (previously identified), were indicated using enrichment techniques.

Direct injection of aqueous essences and aroma samples, using hydrogen flame ionization gas chromatography, has provided rapid and highly sensitive analyses of fresh materials.

Comparative studies have been conducted between volatile flavor constituents of juices of different varieties of oranges. The changes in relative concentrations of components with advancing maturity have also been investigated.

The role played by the major volatile constituents, and the modifying effects of the minor constituents, on the flavor and aroma of citrus juices as determined by physical, chemical, and organoleptic testing should provide a useful characterization of citrus flavors.

## DISCUSSION

Question: Bisulfite will not remove all carbonyls? At best aldehydes and some methyl ketones?

Mr. Wolford: We tested the bisulfite procedure employing well-buffered solutions on synthetic mixtures of aldehydes, ketones, and esters. Following treatment, both gas-liquid chromatographic and infrared analyses showed the absence of carbonyls but did show the presence of the esters. Infrared analyses of methylene chloride extracts of aqueous orange essence, before and after bisulfite treatment, showed no carbonyl absorption. Employing the bubbler technique using 2,4-dinitrophenylhydrazine on eluted components from the gas chromatographic analysis of the same extract produced no turbidity, indicating the absence of carbonyls.

Question: Are the alcohols and acids present as such or as esters?

Mr. Wolford: The alcohols and acids we have identified have been shown to be free and not as esters. The alcohols were obtained by separation on an activated alumina column. Identifications were made by gas chromatography and by paper chromatography and infrared analyses of their urethan derivatives. A fraction containing esters and terpenes was separated, purified, and analyzed by gas chromatography. Tentative identification of some 22 esters was obtained. The esters were not affected by the separation and purification procedures. The identification of the free alcohols and volatile acids are incorporated in a paper to be presented at the American Chemical Society meeting in Los Angeles next week by my coworker, Dr. Attaway.

Question: Do you have any information concerning selectivity of extraction by $CH_2Cl_2$?

Mr. Wolford: We have been striving for a selective solvent for use in these studies. Methylene chloride is not a selective solvent but has provided us with efficient extractions of higher consistency. The aqueous essences are extracted twice with methylene chloride after saturation of the aqueous material with sodium sulfate. The second extraction yields less material in the organic phase than the first extraction. If the water phase is subjected to a third extraction, little or nothing is obtained. We have also studied diethyl ether, isopentane, and chloroform in the early stages of these studies and by comparison prefer the methylene chloride.

Question: Do you have any information concerning possible deterioration of components using vapor phase chromatography analysis?

Mr. Wolford: This is always a concern with gas chromatography. For example, linalool can be dehydrated at 175° C. and is subject to isomerization. We have studied G-L-C patterns of linalool and some of the prominent terpene hydrocarbons at injection temperatures from 50°-250°. Using temperature-programmed gas chromatography, we find an injection temperature of 185°-200° satisfactory without observed deterioration of components. We have not encountered any change in component composition using Carbowax or the other phases we have studied. So far we have no indication of degradation with our VPC methods.

Question: What liquid phases and solid supports are being studied for direct injection of aqueous essences?

Mr. Wolford: Direct injection of aqueous essences has been carried out on Carbowax 20M, DEGS (diethylene glycol succinate), Igepal (nonionic), and Apiezon L. Carbowax 20M in columns 1/4" x 12' and 1/8" x 6' and 10' at coating levels between 4 and 20 percent have been employed. A 10 percent Carbowax 20M, 1/8" x 6' column following thorough conditioning has been giving good resolution of components from aqueous essences using flame ionization detection. Decomposition of Carbowax by water has not been pronounced using low volume injections, normally 1 µl of aqueous essence.

Question: Don't you think that the sugar:acid ratio has a lot to do with flavor in orange varieties?

Mr. Wolford: Yes, I do. The sugar:acid ratio probably influences the flavor perception of orange varieites owing to the sweetness or sourness factors. The flavor differences between varieties at low maturity levels, when the sourness factor is greater, are not as noticeable as when the juice becomes sweeter at maturity.

Question: Would you comment on your methods for overcoming the problem of bleeding of liquid phases at the end of your programmed separations--as it affects identification procedures, IR (infrared) mass spectrograms, etc.?

Mr. Wolford: We have not had a mass spectrograph and, therefore, have no information on the effects of column substrate bleed on this type of analysis of high boiling cuts. In IR analysis, we undoubtedly have a small amount of substrate impurity, but it is not enough to affect infrared resolution.

Question: Are those alcohols and acids in the volatiles naturally present, or are they hydrolysis products of their esters? I notice that linalyl esters are especially unstable.

Mr. Wolford: The alcohols and acids we have found are free materials. This appears to be a continuation of the same question answered earlier. There has been no indication of these alcohols and acids being hydrolysis products. We have attempted to recover the ester fraction *in toto* and have carefully looked at the acid and alcohol moieties. Linalyl esters injected at controlled temperatures, outlined earlier, give single peaks with no decomposition products indicated.

Question: Can you tell us something about the ratio of geranial/neral in orange juice? These are two geometric isomers of citral.

Mr. Wolford: Normally, the geranial has been observed in slightly higher concentration than the neral. Based on relative peak heights on Carbowax 20M, the concentration of geranial is greater than that of neral.

Question: What kind of essence recovery system was used--stripping and fractionation or absorption?

Mr. Wolford: The volatile component stripping system I referred to is the one used at the Citrus Experiment Station. It is a vacuum stripping system composed of a flash chamber and two refrigerated condensers. The all-stainless-steel system operates essentially on the basis of establishing temperature differential between the condensers. By proper balance an essence approximately 100 times the concentration of that found in fresh orange juice is obtained. At the present time we are trying to determine operational characteristics of the system and why it works in the manner described.

# SOME INVESTIGATIONS OF THE CHEMISTRY OF FLAVOR

by

Emily L. Wick
Department of Nutrition, Food Science & Technology
Massachusetts Institute of Technology

Volatile food constituents which serve as taste and odor stimuli have fundamental biological importance. They determine in large part whether foods will be eaten. If responses evoked by such stimuli are not appropriate, foods will not be accepted in spite of their nutrient content. The ultimate goal of basic flavor research is to establish the identity of the stimuli responsible for the characteristic flavor of foodstuffs and to determine the chemical or biochemical mechanisms of their production. This knowledge will contribute significantly to man's understanding of flavor and his ability to measure and control this important biological but nonnutritive property of all foods.

Volatile constituents have been isolated from certain natural and processed foodstuffs as "concentrates" which plainly exhibited the characteristic odor of the material from which they were derived. Their yields were: From ripe bananas, 12-18 p.p.m.; from ripe tomatoes, 3-5 p.p.m.; from fresh bread, 62-100 p.p.m. (or 6-10 p.p.m. on an ethanol-free basis); from beef, 34 p.p.m.; and from irradiated beef, 36 p.p.m. Separation of the "concentrates" by isothermal and temperature-programmed gas chromatography and investigation of the resulting individual fractions has resulted in the identification of many of the major components. These compounds represent only a portion of the volatile constituents known to be present. Their individual biological activity (effectiveness as odor stimuli) is not yet known; but evidence is strong that constituents, as yet unidentified, bear major responsibility as odor stimuli. Results of these investigations are reviewed.

## DISCUSSION

Question: Is there any possibility of correlating a gas chromatogram with adsorption theories in respect to the identified components at receptor surfaces?

Dr. Wick: I don't know. There are theories of adsorption but there is no knowledge of what actually happens in olfaction. This has not been worked out; there is still much to be learned. A correlation may exist, but I don't believe a correlation can be made at this time.

Question: Do you know if anyone has reproduced an aroma by mixing the identified components shown in a chromatogram?

Dr. Wick: I don't know. Perhaps it has been done. Maybe Dr. Ryder can answer this question.

Dr. Ryder: Undoubtedly a great deal of work is being done along these lines. Synthetic duplication of natural aromas was accomplished with varying degrees of success in the perfumery and flavor industries long before the advent of gas chromatography. Now, this refined analytical tool is aiding the compounder by providing information on the chemical composition of natural aromas, allowing an evaluation of the aroma significance of individual aroma components, and has led to the identification and use of specific compounds to achieve specific efforts in the re-creation of natural aromas. Gas chromatography thus provides an excellent means of correlating components individually and in combination with a natural aroma.

Question: What is the best method of determining the role of individual compounds to the odor of a food?

Dr. Wick: Dr. Ryder told how they were correlating peaks or individual components isolated by gas chromatography with odors. I think that is the best method.

## THE RELATION OF MOLECULAR SPACIAL CONFIGURATION TO FLAVOR AND PHYSIOLOGICAL PROPERTIES

by

Carl Bordenca
Manager of Research & Development
The Glidden Company

Many naturally occurring materials exist in different molecular forms which exhibit unusual properties by virtue of the ordered arrangement of their atoms. This phenomenon of isomerism is discussed in the specific cases where differences are due to spacial arrangements and optical and other physical properties are involved.

Examples are given of structurally related materials which differ in flavor, taste, and other physiological characteristics. Consideration is given to the sources of these materials and factors involved in their isolation or production.

It is pointed out that the relationship between molecular spacial arrangements and flavor remains to be established.

## SPECTROMETRY IN IDENTIFICATION OF FLAVOR COMPONENTS; APPLICATION TO SMALL SAMPLES

by

R. M. Silverstein
Stanford Research Institute

What does the flavor chemist do with a milligram or less of a pure, completely unknown compound which he has been able to isolate by gas chromatography? His classical training in qualitative organic analysis is certainly inadequate for the task in hand.

This discussion is concerned with identification of small amounts of pure organic compounds by means of four energy probes. The responses of the molecule to these probes are recorded as spectra. We are concerned with the following kinds of spectra: Mass, infrared, NMR, and ultraviolet.

These four spectra give data that are complementary. Only a modest degree of sophistication in each of these areas of spectrometry will solve a gratifying number of problems.

For most materials that can be passed through a gas chromatographic column, no other information is necessary. We dispense with physical properties, elemental analyses, and derivatives. For more complex materials, degradations can be carried out, and the energy-probe methodology applied to the degradation products.

[Familiarity on the part of the audience with IR, NMR, and UV is assumed. Some aspects of mass spectrometry are briefly reviewed, and the steps required to establish an exact molecular weight and an empirical formula are traced.]

[A problem is presented and worked out.]

## DISCUSSION

Question: About how much would it cost to identify a compound in the manner you described?

Dr. Silverstein: Cost can be measured by a comparison of classical procedures with more modern instrumental techniques. If it is a straightforward case, classical techniques may be used for identification. Methods requiring spectrophotometry and G-L chromatography would have to take into account costs of instruments. But with a straightforward case this can be done cheaper since technicians can be used to perform the bulk of instrumental analyses. Spectrometry allows the average chemist today to accomplish what the genius of yesterday had done by using classical techniques. If the problem is simple and uncomplicated, a one mg. sample should be sufficient for determination of the spectrophotometric properties I duscussed. It would take about 1 hour of each technician's time, or a total of 4 hours time for identification.

## PROGRESS AND LIMITATIONS IN THE IDENTIFICATION OF FLAVOR COMPONENTS

by

William S. Ryder

General Foods Corporation

Several limitations of the technique of gas chromatography have been recognized in the analysis of food flavors. These include the necessity for sample preparation, incomplete resolution of components, creation of artifacts, adsorption losses, and insufficient sensitivity. These, along with the fact that gas chromatography is not an identification, techniques are not new in themselves, but any one of them can be a serious problem in the determination of flavor composition. Recent advances in the technique of gas chromatography allow one to eliminate or minimize these difficulties to a great extent.

Retention-time data obtained by gas chromatography under specific analytical conditions coupled with detailed odor evaluations provide information used in the creation of appealing imitation flavors and in the quality control of raw materials and food products during processing and through storage.

Special techniques of gas chromatography applied to the analysis of headspace vapors over a food ingredient or product provide a graphic picture of the composition of the vapor encountered by tasters. Differences among headspace aroma patterns may agree very closely with taste panel evaluations and may be used in a number of situations to reflect both good and bad flavor characteristics.

Techniques for the chemical separation of classes of flavor compounds have been employed to advantage in the analysis of complex flavor extracts. A time-of-flight mass spectrometer used as the detector for a gas chromatographic column, provides the fastest and most direct means for the identification of individual flavor components. Infrared and NMR spectrometry are extremely useful for the identification of flavor components and providing proof of chemical structure. Because of their relatively low order of sensitivity and long scan time, these supporting instrumental methods of analysis are reserved for specific individual flavor components.

## DISCUSSION

Question: Can aroma be exactly duplicated on basis of flavor introduced?

Dr. Ryder: Tentatively, yes. Using an "artistic" approach to compounding, many natural aromas can be duplicated from analytical data on chemical composition. The chemist doing the compounding work should be prepared to take a few liberties with the analytical data. Not every identified compound need be used in the synthetic formulation. Depending upon the degree of sophistication required, a natural flavor concentrate containing approximately 100 components may be satisfactorily duplicated with 10 to 20 compounds. The quantitative relationships among individual components in the flavor concentrate may have to be altered somewhat in order to achieve a more appealing synthetic blend.

Many of the compounds which occur as constituents of natural flavors are not available from commercial sources. Here is where the synthetic organic chemists help us out. Using data from gas chromatography and from infrared, mass and nuclear magnetic resonance spectrometry, they can synthesize these unique compounds, which can then be evaluated individually and as components of synthetic formulations.

I do not mean to imply that this is a simple and straightforward process. Frequently the data obtained do not provide enough information for the flavor chemist. This, however, usually means that there was something wrong with the manner in which the natural flavor concentrate was prepared or with the manner in which it was analyzed. I think it has been the general experience that fruit and floral essences are better suited to the scheme of analysis and duplication than other types of flavors. This may be because of their inherent composition, i.e., concentration, number of constituents, chemical type, and chemical stability. Much of our interest in flavors lies in the nonfruit areas and there is a great deal of work that needs to be done.

Question: What tubing can be used in a squeegee pump without introducing or removing volatiles?

Dr. Ryder: Surgical gum rubber tubing can be used. Whatever type you are using should be checked carefully to make certain you are not getting unusual results from tubing employed. Wash the gum rubber tubing well and purge it well. It must not contribute or take out any volatile materials.

Question: Which of the three essence recovery processes gives the best essence: (1) Ed-Milleville process reported by Veldhuis; (2) the Lake Alfred process reported by Wolford; and (3) the one you (Dr. Ryder) described? Which process should be used? Is scale of operation or efficiency of recovery important in the selection?

Mr. Wolford: Some of the differences between our process and Dr. Veldhuis' process have been explained. The chromatograms from volatiles supplied by both systems showed similar patterns. Veldhuis' process was used by Dr. Gold and is reported in his paper. I am not aware that the three methods have been compared as to efficiency. As a matter of need the process described by Dr. Veldhuis was designed to handle small volumes in the milliliter range while our system requires large quantities of juice in the 50- to 100-gallon range.

Question: How would the VPC of your essence-recovery process compare with the one reported by Veldhuis recently?

Dr. Ryder: The gadget we had was a small-scale laboratory set-up. These gentlemen are talking about obtaining gallons of material per minute. You are talking about two different things. We have not scaled up our equipment to handle fast input and volume recovery. We have not had gallons running through; in fact, we have been satisfied getting milliliters for analysis. We have not needed larger volumes of recovered material for our work.

Mr. Wolford: At the Citrus Experiment Station we are dealing with very low concentrations of material, therefore larger volumes of juice must be handled for sufficient recovery of the small amounts of volatile components. The vacuum stripping system which we have should have at least 50 gallons of juice for startup. The system consists of two Freon condensers which can be adjusted for the appropriate temperature differential. The juice is brought to 150° F. and is introduced rapidly into a flash chamber under high vacuum at about 80°. Vapors moved to the higher temperature condenser (78°) are constantly being refluxed. The volatile materials then move to the 30° condenser where they are condensed. The system is very sensitive to the temperature differential established. The output can be boosted by varying the temperature differential between the columns within fine limits, thus producing higher or lower concentration of volatiles dependent upon the output volume.

## THE VOLATILE FLAVOR SUBSTANCES OF CELERY

by

Harvey J. Gold and Charles W. Wilson, III
U.S. Fruit and Vegetable Products Laboratory

[Presented by Dr. Gold]

Preliminary experiments on the flavor of celery established that the concentration of recoverable volatile materials in celery juice was on the order of 1 p.p.m., necessitating the use of large quantities of starting material. A total of about 10,000 pounds of celery was used in these studies. Recovery of the volatile materials was accomplished by vacuum distillation of the juice in a pilot-plant essence-recovery unit.

The number of compounds in each distillate fraction ranged from four to thirty. Simpler fractions were submitted directly to gas chromatography. The more complex systems were fractionated by the use of functional group reagents and silica gel chromatography, before the final separations on the gas chromatograph. These procedures simplified the gas chromatograms obtained, facilitating interpretation and collection of individual components. Much valuable information was gained by the use of spot-test techniques and by the technique of subtractive gas chromatography.

In most cases, identifications were based upon comparison of both infrared spectra and gas chromatographic retention times with those of authentic compounds. In some cases, where sufficient material was not available for detailed study, tentative identifications were made based upon GLC retention time and knowledge of the functional group. Thirty-five compounds were identified, and 11 compounds were considered to be tentatively identified.

Three additional compounds, all of which were found to be intimately concerned with the flavor of celery, were new substances. Structural elucidation of these compounds were made using, in addition to various chemical techniques, infrared, ultraviolet, and mass spectrometry.

The following six compounds were found to be the ones primarily concerned with the flavor of celery: 3-isobutylidene-3a,4-dihydrophthalide; 3-isovalidene-3a,4-dihydrophthalide; 3-isobutylidene phthalide; 3-isovalidene phthalide;

cis-3-hexen-1-yl pyruvate; and diacetyl. By recombination of the isolated compounds, it was possible to reproduce the flavor and odor of celery.

Present studies are concerned with changes taking place during processing of celery, particularly dehydration. These changes are being followed by gas chromatography of headspace gases.

## DISCUSSION

Question: How many milligrams of material did you isolate from the 10,000 pounds of celery?

Dr. Gold: The two aromatic phthalide, as I recall, were in amounts of 4 to 5 mg. each. The isobutylidene dihydrophthalide was in the range of 30 to 35 mg., and the isovalidene dihydrophthalide was in the range of 30 to 35 mg., and the isovalidene dihydrophthalide was obtained in the amount of about 15 mg. A few milligrams each of the pyruvate and of diacetyl were isolated. It was possible to use commercial celery seed oil as an additional source of the dihydrophthalides. In compounding celery flavor, we found that the best formulation consisted of 26 parts of isobutylidene-3a,4-dihydrophthalide, 13 parts of 3-isovalidene-3a,4-dihydrophthalide, 4 parts of cis-3-hexen-1-yl pyruvate and 1 part of diacetyl.

Question: Will the same compounds be found in oil of celery as are found in the juice of fresh celery?

Dr. Gold: I can partially answer this question. We did not run any detailed study. The flavor of oil from celery seed is quite different from that of fresh celery. Guenther reports what is known about the composition of seed. He cites sedanonic anhydride and secanolide as the main flavor components. Results of our chromatography and IR data show that other materials are also involved in the flavor of celery seed oil.

Question: How difficult is it to open the lactone in your aromatic phthalides?

Dr. Gold: I don't know. We never tried this on the aromatic phthalides. With the dihydrophthalides it is very hard to accomplish. In using the sealed-tube technique, the free acid can be obtained in small yield after prolonged heating. It easily reverts to the parent.

Question: Have freeze-concentration methods been used to concentrate these juices prior to fractionation, etc.?

Dr. Gold: Dr. Dennison at Gainesville has used that procedure. Initially we used some of Dr. Dennison's material and we could detect no qualitative differences between the freeze-concentrated and single-strength juice.

Question: What test method was used to test the similarity of your mixtures with V-8 juice?

Dr. Gold: I didn't say V-8. We made a blend of tomato juice and celery juice and sought to duplicate the flavor with a synthetic blend of tomato juice and the isolated celery flavor constituents. One fellow said that the synthetic mixture contained too strong a flavor of celery.

Dr. Silverstein: I just want to pay a compliment to Dr. Gold, who employed a mixture of classical techniques and new techniques to work out the complicated structures of the flavor materials of celery in an excellent work of research.

## CHEMISTRY OF MEAT FLAVOR

by

Irwin Hornstein
Meat Laboratory
Eastern Utilization Research and Development Division
Agricultural Research Service

The precursors of the volatile contributors to lean-meat flavor are water extractable. Lyophilization of these extracts yields water-soluble powders. These powders have been refluxed in water and heated in air and the aromas have been evaluated for flavor contribution. Species differences were not detectable in the volatiles; the same basic meaty aromas were obtained from lamb, pork, and beef. Heating these powders under vacuum yielded a meaty volatile fraction that was trapped at liquid-nitrogen temperature and further fractioned under vacuum. The substances in these fractions have been separated chromatographically and studied spectrophotometrically. Again lean beef, pork, and lamb yielded surprisingly similar results. The lean-meat flavor precursors were separated on the basis of size both by dialysis and sephadex-gel filtration; the low molecular-weight fraction contained the flavor precursors, and lyophilization of this fraction yielded a rather unstable white fluffy powder that, on vacuum pyrolysis, gave patterns of odors and compounds similar to those obtained from the initial water extracts. The white powders were separated into amino acids and a neutral subfraction containing sugars; heating these subfractions did not produce meatlike aromas. Recombination of the subfraction followed by heating produced the meaty aromas.

Species differences were found to reside in the fat of beef, pork, and lamb. Characteristic beef and pork aromas were obtained from fat heated in air but not under vacuum or nitrogen. Characteristic lamb flavor could, however, be obtained from lamb heated in nitrogen or in air. Major qualitative and quantitative differences exist in the free fatty acids and carbonyl compounds present in these fats both before and after heating in air or nitrogen or vacuum. Further studies on lamb fat have shown that the characteristic lamb flavor is not a product of fatty acid oxidation but is carbonyl in nature and presumably present as a lipid soluble material in the fat.

Phospholipids in lean meat were extracted and separated into lecithins, cephalins, and sphingomyelins and their fatty acid composition determined.

An evaluation of phospholipid contribution to flavor indicated that these compounds contributed to off-flavor more than to desirable flavor.

It has been concluded that lean meats contribute a similar basic meaty flavor and that species flavor differences reside in the fat. Profound effects on flavor may be exerted by extraneous materials stored in the fat, as is apparently the case in lamb. A study on whale meat has also indicated that the lean, which is essentially an aqueous phase, may also act as a reservoir for water-soluble compounds that may affect flavor.

## DISCUSSION

| | |
|---|---|
| Question: | Do you have any basic chromatographic system? |
| Dr. Hornstein: | We used, in the main, paper chromatography to determine carbonyl compounds and amines; column chromatography to separate total lipid extracts from muscle; and gas chromatography to determine fatty acids, to isolate compounds, and to compare patterns of volatiles from different animals and species. |
| Question: | How did you esterify acids on the exchange column? |
| Dr. Hornstein: | We did not use an exchange column; we used a batch method. Fat dissolved in petroleum ether was stirred with a batch of Amberlite IRA-400 (OH form). The free fatty acids were adsorbed on the resin, and the triglycerides in the petroleum ether solution were removed by decantation. The resin was washed free of fat with petroleum ether and the adsorbed acids were converted to their methyl esters and simultaneously eluted by stirring the resin with anhydrous methanol-hydrochloric acid. This solution was then diluted with water and the esters extracted with petroleum ether. |

## GAS CHROMATOGRAPHIC STUDIES ON VOLATILE COMPOUNDS FROM PROCESSED TOMATOES

by

Richard E. Hein and Gordon W. Fuller
Mellon Institute

[Presented by Dr. Hein]

Published reports of investigations of volatile compounds responsible for the odor and flavor of the tomato are very few in number. The literature indicates that progress in this area of research has lagged behind that achieved with other foods, in general, and other fruits, in particular. This situation is not necessarily a result of a lack of interest in the topic; rather the tomato system presents the investigator with problems which tax present methods of extraction, concentration, separation, detection, and identification quite heavily.

Spencer and Stanley (1954) found that the compounds contributing to the total tomato odor were many in number, covered a wide boiling-point range, were present in low concentration (about 2 p.p.m.), and apparently were subject to heat or oxidation damage. Three general types of odor fractions (green, raw, and tomato) were isolated by column chromatography. The typical tomato odor fraction contained alcohols, carbonyl compounds, and unsaturates. The probable presence of citral and terpenelike compounds indicates some similarity between tomato and citrus flavor components.

In an extensive study by Pyne and Wick (Ph.D. thesis by Pyne, 1962) on volatile components of fresh tomatoes, these investigators reported the concentration of total volatile components was in the 3 to 5 p.p.m. range. Twelve components not previously known to be constituents of tomatoes were rigorously identified. Most of the volatile components were alcohols with cis-3-hexenol-1 (leaf alcohol) present in the largest amount.

Extracts of condensate from large-scale vacuum evaporation of thin pulp and solvent extraction of the resulting tomato paste are the two principal sources of tomato odor fractions in our work. In preliminary studies in 1960, gas-chromatographic examination of concentrates from the two aforementioned sources showed that each contained the same components, with the tomato-paste extract having a greater proportion of the higher boiling components. A number of compounds were tentatively identified which have also been found in citrus fruits.

Present studies are concerned with an extension of the previous work and particularly with the gas chromatographic analysis of condensate from vacuum evaporation of hot-break (enzyme inactivated) and cold-break (low pectin) tomato paste. A progress report on these studies will be given.

## DISCUSSION

Question: Are the chromatograms of freshly pressed tomato juice, cold-break and hot-break tomato paste, similar?

Dr. Hein: Differences were observed in the relative quantity of components in the volatile fractions from cold-break and hot-break tomato paste. No major component or peak was found in the concentrate from one process and not in the other. Whether the differences observed in relative concentration are real or a function of the concentration and extraction steps will have to be determined by further study. We have not studied the volatile components in freshly pressed tomato juice.

Question: Where does the "green" buildup show in fresh pressed juice? Does it build up as strongly as the powdered products? Were you able to inhibit formation of "green" compounds?

Dr. Hein: The "green" note in tomatoes can be attributed at least in part to the presence of cis-3-hexenol-1 (leaf alcohol) and one or more of the hexenols. This "green" or "viney" fraction is present normally, is relatively volatile, and is diminished in concentration steps where water is removed as in flashing operations. Hence, it probably would be less noticeable in a concentrated product such as tomato powder. So far as inhibiting formation of the "green" compounds, it presumably is not formed by any enzyme action on breaking of the tomato and hence is already present in the tomato. Again, the control of the relative amount of this compound would probably depend on some concentration step whereby the more volatile components are removed.

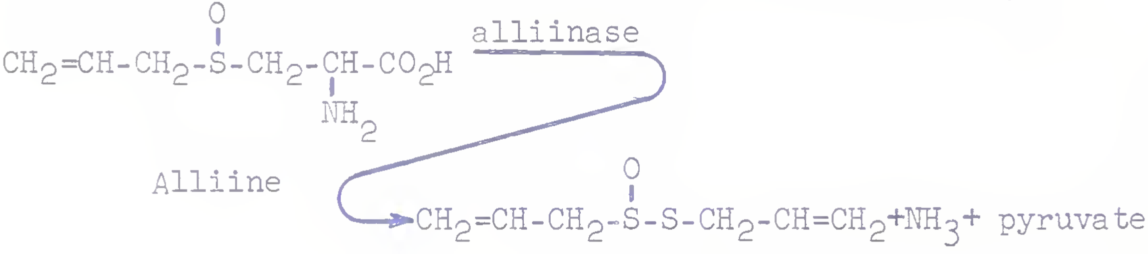
## STUDIES ON THE FLAVOR OF ALLIUM

by
R. A. Bernhard
Department of Food Science and Technology
University of California

The genus Allium provides an interesting source of many sulfur compounds and reveals much that is both novel and complex in sulfur chemistry. It is now generally accepted that a number of these sulfur-containing compounds contribute extensively to the characteristic flavor and aroma of members of this genus, e.g., onions, garlic, leek, chive, rakkyo. Very little is known about the chemical composition of members of this genus. The common onion (Allium cepa) and garlic (Allium sativum) have been investigated more extensively than the other members, but much remains to be clarified. For example, the precise chemical nature of the lachrymatory principle in onion is not known.

It is known that derivatives of the amino acid cysteine are precursors of many of the important sulfur compounds found in Allium. One such compound alliine (S-allyl cysteine sulfoxide) is the precursor of allicin (diallyl thiosulfinate). When alliine is treated with alliinase, a crude enzyme preparation obtained from garlic, allicin is formed together with pyruvic acid and ammonia. The resulting thiosulfinate can then undergo a disproportionation reaction to form a thiosulfonate, a disulfide, $SO_2$, and a polymer of unknown composition.

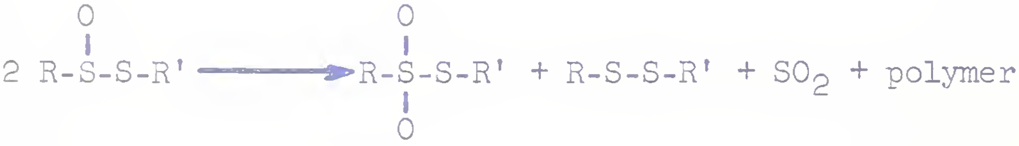
The scheme for this series of reactions is as follows:



$$CH_2{=}CH{-}CH_2{-}\overset{O}{S}{-}CH_2{-}\underset{NH_2}{CH}{-}CO_2H \xrightarrow{\text{alliinase}} CH_2{=}CH{-}CH_2{-}\overset{O}{S}{-}S{-}CH_2{-}CH{=}CH_2 + NH_3 + \text{pyruvate}$$

Alliine

Allicin



$$2\ R{-}\overset{O}{S}{-}S{-}R' \longrightarrow R{-}\overset{O}{\underset{O}{S}}{-}S{-}R' + R{-}S{-}S{-}R' + SO_2 + \text{polymer}$$

Thiosulfinate Thiosulfonate disulfide

These reactions can be demonstrated to occur *in vitro* and undoubtedly occur *in vivo* when members of this genus are subjected to tissue damage as happens with cutting or slicing. It is interesting to note that garlic tissue has virtually no odor until it has been injured and its structural integrity destroyed. The formation of volatile disulfide compounds is presumed to be one of the principal sources of the characteristic flavor and aroma of garlic, and indeed, all members of the genus *Allium*. It thus appeared reasonable to assume that there should be marked differences in the disulfide composition of each species within the genus that could account for the varied flavors and aromas of the individual members, and that examination of these might give considerable insight as to the flavor constituents of *Allium*. In addition, it should be possible to use this knowledge of disulfide distribution to improve the systematics of the genus, since it can be presumed that plants with similar chemical composition are closely related.

Disulfides were isolated from various plant tissues and tentatively identified by gas chromatographic analyses and retention volume data. The individual disulfides were then isolated in greater amounts and subjected to infrared analyses. Additional material was then analyzed for carbon, hydrogen, and sulfur content, and the empirical formulae established. As a further check on identity, the disulfides were synthesized by accepted chemical means and their properties checked by infrared analyses; carbon, hydrogen, sulfur analyses; and gas chromatographic analyses. These known compounds were then compared with the disulfides isolated from various plant tissues. Thus, the identity of the isolated compounds was well established.

To date, some 10 *Allium* and 2 *Tulbaghia* species have been extensively examined to determine the distribution of the disulfides within these plants.

From this work it now seems certain that various substituted S-alkyl and S-alkenyl cysteine sulfoxides are present in various *Alliums* and related genera.

The alliine of *Allium sativum* contains allyl radicals, from which is derived the pungent diallyl disulfide of garlic, and methyl allyl disulfide. In addition, there is also some allyl sulfide and a small amount of methyl disulfide in garlic. Thus, the allyl moiety can be associated with the characteristic flavor of garlic. In contrast, *A. cepa* contains mostly propyl disulfide and methyl propyl disulfide, but no allyl compounds. The addition of two hydrogen atoms modifies the aroma to a considerable extent. Those species that contain large amounts of methyl disulfide have a characteristic cooked-cabbage aroma. These differences, at least in part, account for the distinctive odors and flavors of these species.

## DISCUSSION

Question: Are the kinetics of sulfide formation the same for onion, garlic, and chive?

Dr. Bernhard: Although we have no precise information on this at the present time, I would suspect the answer to be no.

# PRELIMINARY STUDIES ON THE FLAVOR OF ROASTED PEANUTS

by
George R. Waller
Department of Biochemistry
Oklahoma State University

About 50 percent of the edible raw shelled peanuts produced and processed in the United States are used in the manufacture of peanut butter. Palatability of peanut butter has been considered the ultimate basis of consumer acceptance. Peanut butter flavor research was begun at Oklahoma State University in 1959 as a cooperative endeavor by the Departments of Biochemistry and Agronomy.

Research was initiated to secure information on peanut butter flavor with emphasis being placed on: (a) isolation and identification of the flavor constituents of peanut butter, (b) organoleptic evaluation of peanut butter samples representing various agronomic practices and genetic differences, (c) agronomic problems involved in high-quality peanut production, and (d) quantitative determination of fatty acids found in peanut oil.

Peanuts that represent the influence of germ plasm, chemicals, and cultural practices used in their production are processed into peanut butter, which is then evaluated organoleptically with respect to their odor and taste using a coded standard (which also served as the reference sample) as the basis for comparison. Results from a test of four Spanish varieties, which were classified as mature or immature on the basis of the outward appearance of the fruit and reclassified on the basis of the interior color of the fruit, confirmed the belief that the mature peanuts are the most desirable. In carrying out organoleptic studies, a higher degree of uniformity of results can be obtained if only mature peanuts are used. Of 23 plant introductions evaluated, the results indicate there may be germ plasm available with superior flavor which should be used in a hybridization program in the production of better quality peanuts for food uses.

Roasting studies performed at different temperatures with three varieties of Spanish peanuts indicate that the development of flavor may be a function of the heat supplied once a certain minimum temperature is reached. The requirement of heat is dependent upon large quantities of precursors being present in the raw peanuts. If intermolecular reactions involved in the formation of flavor are minimal, then isolation of flavor precursors as individual components should be possible using a procedure which destroys the cellular integrity of the peanut. A process which involves defatting, grinding, and extracting the raw peanuts in 1 M NaCl followed by development on columns using Sephadex Gel permitted the isolation of a fraction responsible for the production of "typical peanut aroma."

The problem of chemically defining roasted peanut flavor has been approached from two different aspects: (a) Development of techniques for the isolation of peanut flavor components and their subsequent separation, identification, and quantitative estimation; and (b) development of techniques for the isolation, identification, and quantitative estimation of the flavor precursors. By use of a high-vacuum degassing procedure on oil pressed from roasted peanuts, a complete deodorization of the oil has been obtained and a gas chromatogram of the mixture of aroma components trapped under liquid nitrogen has been made. Mass spectrometric analysis of this mixture has led to some tentative identifications of components. Attempts to obtain individual components using preparative gas chromatography have met with limited success.

## SUMMARY REMARKS ON CONFERENCE

by

M. K. Veldhuis

U.S. Fruit and Vegetable Products Laboratory

This conference has been a most valuable one. Each paper presented has been very good. I should like to congratulate the Experiment Stations, The Southern Laboratory, Dr. C. H. Fisher, Mr. E. L. Patton, and all who took part in preparing such an excellent conference for us. This is the golden era of flavor research, like the beginning of the century for the microbiologist. There are endless opportunities on hand for research on flavors. There are many tools on hand for studying flavor constituents, and we have become acquainted with many of them through the discussions presented here in these 2 days.

Dr. Peryam of the Quartermaster Command of Chicago presented an excellent discussion of psychological methods for measuring flavor effects. Organoleptic flavor evaluation remains the primary method of determining quality in foods and will remain the standard of reference.

Mr. Downey pointed out the work on basic flavors. He noted a demand for basic flavors such as wheat, corn, and rice. He voiced the opinion that work on metabolic pathways would permit the selection of food and flavor products of optimum quality.

Mr. Wolford reviewed the work of the Florida Citrus Commission on flavor components of citrus juices. Out of 55 components, 29 have been identified by infrared spectra or equal, and 14 more have been tentatively identified on the basis of retention time on at least 2 G-L-C columns. All were impressed with the complexity of the G-L-C presentations and the difficulty in evaluating the importance of the various peaks.

Dr. Emily Wick gave a very fine discussion of the chemistry of flavor. She pointed out that the gas chromatograph responded to the amount of a constituent present and not necessarily in proportion to the importance of this constituent to flavor. She outlined the immense task in evaluating the importance of the compounds already isolated, in addition to those not identified.

The spacial configuration of molecules and their relation to flavor was discussed by Dr. Bordenca. Optical isomers can differ widely in flavor. For example, l-carvone is like spearmint and d-carvone is like oil of caraway, while d-limonene is citruslike and l-limonene is less intense and rather flat in aroma. Citral-a and citral-b also differ in aroma.

Dr. Silverstein worked with the audience and showed how benzylacetate could be identified using data from mass, NMR, UV, and IR spectra. He showed how easily identification can be carried out with a laboratory as well equipped as his with personnel and instrumentation. I hope all of you could follow his discussion about the very latest methods for identification, and arrived at the same conclusion about the test compound he gave us to identify. This reminds me of the story of the two surgeons, and after the operation one turned to the other and said, "One inch either way and I would have been out of my field."

Dr. Ryder iterated about UV, NMR and IR studies for resolving more complicated G-L-C curves. He told of how two chromatographic columns with different packing were charged and operated simultaneously from a single sample injection. He indicated that a careful selection of conditions minimized the development of artifacts in G-L-C columns. He also discussed electron capture.

Dr. Gold gave a very able picture of the chemistry of celery flavor, and had to work up 10,000 pounds of celery for a few milligrams of materials, and that was a feat in itself. He had a very difficult task because the materials he had to identify occurred in amounts of below 1 p.p.m. in starting material. Gold demonstrated that six components are responsible for celery flavor.

Dr. Hornstein discussed meat flavors. His problem was a different "kettle of fish" from the usual green-stuff problems discussed previously. He found the characteristic flavors among the water-soluble rather than among the fat-soluble components. He showed an excellent following through of his problem and reported on several interesting approaches used in tying down the flavors of meat. The often mentioned carbonyls were listed again as being important to flavor as were the fatty acids.

Dr. Hein discussed G-L-C of tomato volatiles. He is confronted with a very complex situation in that the materials he is working with occur in the range of 2 p.p.m. source material. Dr. Bernhard told us about his interesting work on the flavor of Allium, and classification of Allium by certain flavor components. Dr. Waller gave a detailed discussion about studies on the flavor of roasted peanuts. I am told that our bus is waiting and I must close, so I turn the meeting back to Dr. Reitz.

Dr. Reitz: Thank you, Dr. Veldhuis. You are to be congratulated on the challenge to summarize this conference.

## APPENDIX

## ATTENDANCE LIST

Albrecht, James J., International Minerals & Chem. Corp., Old Orchard Rd., Skokie, Ill.

Appl, R., Corn Products Co., P.O. Box 345, Argo, Ill.

Aurand, Leonard W., Dept. of Food Science, North Carolina State Coll., Raleigh, N. C.

Baumgardner, R. A., Dept. of Hort. & Lands. Arch., Louisiana State Univ., Baton Rouge, La.

Bennett, W. B., U.S. Tobacco Co., 905 Harrison St., Nashville, Tenn.

Bernhard, Richard A., Dept. of Food Sci. & Technol., Univ. of California, Davis, Calif.

Bone, David, Quaker Oats Co., 617 West Main St., Barrington, Ill.

Bordenca, Carl, The Glidden Co., P.O. Box 389, Jacksonville 1, Fla.

Breithaupt, Lea J., International Paper Co., Mobile, Ala.

Brittin, W. A., Spice Res., Wm. J. Stange Co., 342 North Western Ave., Chicago 12, Ill.

Brown, Leo C., Derby Foods, Inc., 2244 West 110th Place, Chicago 43, Ill.

Burk, Earl F., Processed Products Inspection, Agr. Marketing Serv., U.S. Dept. of Agr., Hammond, La.

Burns, E. E., Soil & Crop Sci. Dept., Texas A&M University, College Station, Tex.

Campbell, Roy E., Northern Util. Res. & Devlp. Div., U.S. Dept. of Agr., 1815 North University St., Peoria, Ill.

Cardwell, Joe T., Mississippi State Univ., P.O. Box 873, State College, Miss.

Cluett, Maxwell L., Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

Dainius, Bill, Research Lab., Wm. J. Stange Co., 342 North Western Ave., Chicago 12, Ill.

Danna, Emile J., Processed Products Inspection, Agr. Marketing Serv., U.S. Dept. of Agr., Hammond, La.

Denton, A. E., Campbell Soup Co., 100 Market St., Camden, N. J.

Deszyck, Edward J., Philip Morris Research, P.O. Box 3D, Richmond 6, Va.

Downey, William J., Fritzsche Brothers, Inc., 76 Ninth Ave., New York 11, N. Y.

Ellis, Barbara Hall, Continental Can Co., Inc., 1350 West 76th St., Chicago 20, Ill.

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1862
1889